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(54) **Separators for Lead Acid
Accumulators**

(57) Separators are manufactured by a paper-making method, sometimes followed by partial melting, from an aqueous dispersion comprising a blend of cellulosic fibers and olefin polymer fibrils in a ratio of from 20:80 to 40 to 60, the blend having a degree

of freeness of from 40 to 75°SR. The blend also contains:

from 20 to 55% of an inorganic powder -substantially insoluble in sulphuric acid;

from 0.01 to 0.3% of an ionic or non-ionic wetting agent;

up to 50%, preferably from 10 to 20% of glass fibres; and

up to 50%, preferably from 10 to 20% of a vinyl or like polymer latex.

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SPECIFICATION Separators for Lead Acid Accumulators

The invention relates to a process of manufacturing separators for lead acid accumulators, and is a development from our Patent Application GB 2,054,251 A.

The process of the invention comprises making an aqueous dispersion of a blend of cellulose fibres and olefin polymeric fibrils, in a ratio of from 20:80 to 40:60, the blend having a degree of freeness of from 40 to 75° SR, from 20 to 55% of an inorganic powdery material soluble in 30% sulphuric acid at 71°C after 72 hours residence to an extent of less than 5%, and from 0.01 to 0.3% of a wetting agent, and forming a sheet from the dispersion by a paper-making method.

The resulting sheets have pores of a very small diameter, a high total porosity and a satisfactory ionic permeability. Unless otherwise stated, or the sense demands, all % herein are by weight with respect to total solids.

The wetting agent may be ionic or non-ionic. The fibrils generally have a surface area of at least 1 sq m/g. After formation, the sheet is generally pressed and then dried. The drying may be followed up by a subsequent dry-pressing, for instance on the glazer of the paper machine, before winding on a reel. The dry weight of the resulting panel is generally from 100 to 250 g/sq.m, and its density from 0.35 to 0.6 g/cu.m.

The dried sheet may be subjected to a consolidation operation which, besides increasing its dimensional stability, renders it particularly resistant to moisture or humidity. Such an operation consists in heating the panel or sheet at a temperature at least equal to the melt temperature of the fibrils. The heating is carried out under the substantial absence of pressure on the sheet, and may be achieved by passing the sheet over the surface of a heated cylinder, or in a hot air tunnel, or by I.R. radiation. The pressure exerted on the sheet should not exceed 0.01 kg/cm if the heating is passing the sheet between a pair of rollers.

However, it is possible to avoid such consolidation and still obtain the desired dimensional stability and resistance to humidity, with the further advantage of favouring the formation of small diameter pores and a higher total porosity, if to the aqueous dispersion there is added up to 50%, preferably from 10 to 20% of a vinyl or vinylidene polymer, an ethylene-propylene copolymer, or a copolymer of a vinyl or vinylidene monomer with ethylene, containing up to 50 mol % of copolymerized ethylene in a dispersed state or in the form of a latex. Such a polymer is then made to coagulate in the aqueous dispersion by acidification before the formation of the sheet.

It has been found, moreover, that it is possible to obtain sheets with good rigidity in spite of the high content of filler, by adding to the dispersion glass fibres up to 50%, preferably from 10% to 20% by weight with reference to the blend. The glass fibres have a diameter not exceeding 15 microns; their length is not critical, although it is preferably from 1.5 to 12 mm.

The sheet may consist of only one layer or of a number of layers of various composition. After the sheets have been dried and/or heated, they may be provided with the necessary spacers, for instance by extrusion directly onto their surface of thermoplastic polymer filaments of suitable dimensions. If the sheets have been subjected to a thermal treatment to melt the polyolefinic fibrils, the application of the spacers may be carried out during the thermal treatment by, for instance, heat welding onto their surface low-density polyethylene filaments containing talc or carbon black fillers. Separators in the shape of small bags or covers may also be obtained from sheets prepared by the process of the invention by hot-welding of the edges.

Examples for inorganic materials that display a solubility in sulphuric acid as previously defined are silica and talc. Particularly suitable is the silica known under the commercial name "Ultrasil VN-2" produced by Degussa. The particle size distribution is generally less than 30 microns, and preferably from 0.02 to 20 microns.

Examples of suitable polymer latices or dispersions are those comprising polyvinyl chloride, polyvinylacetate, polyvinylalcohol, polystyrene, polyvinylidene chloride, methyl polymethacrylates and methyl polyethylacrylates, ethyl, propyl, isopropyl, butyl and isobutyl, polyacrylonitrile methacrylates and ethylacrylates, copolymers of such methacrylates or ethylacrylates with acrylonitrile, acrylic acid or methacrylic acid, acrylamides or with mixtures thereof, and ethylene copolymers with the vinyl and/or vinylidene monomers corresponding to the said vinyl or vinylidene polymers.

The olefin polymeric fibrils in general have a length of from about 1 and 10 mm, a mean diameter of between 1 and 50 micron. They may contain incorporated inorganic fillers such as talcs, cadmium, silicon or titanium dioxide, barium sulphate, in quantities up to 60% by weight on the total weight of the fibrils. Olefinic polymers from which the fibrils may have been obtained, are for instance: low or high density polyethylene, polypropylene prevailing consisting of isotactic macromolecules, poly-4-methylpentene-1, ethylene-propylene copolymers, and the mixtures of such polymers and copolymers.

The possible thermal treatment of the sheet which melts at least part of the fibrils is preferably carried out at a temperature greater by at least 5 or 10°C than the melt temperature of the constituent polymer, or of the constituent polymer with the lowest melt temperature if the fibrils are made of different polymers or of mixtures of such polymers. If the sheet has been prepared from dispersions

containing latexes, it is advisable to avoid thermal fusion treatment of the fibrils. It is actually sufficient to dry the sheet at a temperature generally of from 60°C to 115°C in order to achieve the advantages due to the presence in the sheet of such a polymer.

- 5 As cellulosic fibres there may be used the type of fibres usually employed in the preparation of papers. Preferably there are used mixtures of cellulose fibres obtained from conifers. 5

Example 1

- 10 A mixture in water of 24.5 kg of high density polyethylene fibrils (having a melt temperature of 135°C, a surface area of 6 sq. m/g, mean length of 3 mm and mean diameter (apparent diameter of 16 micron) and 10.5 kg of cellulose fibres of bianchita conifera was refined in a conical refiner at a concentration of 2.5% by weight, up to 74° SR (Schoppe-Reigler). This blend was mixed with 10 kg of glass fibres having a diameter of about 10 micron and a length of 6 mm, and 40 kg of silica (Ultrasil VN-2). After homogenization, the mixture was diluted with water up to 0.6% by weight solids. It was then mixed with 30 kg of DR-1465 (a 50% by weight latex of a tetrapolymer of butyl acrylate, styrene, a methylol derivative of methacrylamide and methacrylic acid, produced by Montedison S.p.A.), and 2 kg of Teepol PG (an anionic surfactant produced by Shell). The dispersion was acidified with a saturated solution of aluminium sulphate up to a pH of 4.5, and was then diluted down to 0.2% by weight solids. From this dispersion there was formed a sheet on a continuous paper producing machine provided with a wet press operating at a pressure of 5.5 kg/sq.cm, and dried at 90°C. The properties of the resulting sheet are set out in a Table at the end together with those of the other Examples. 15

20 Example 2

The same preparation as in Example 1 was repeated with the difference that on the continuous paper machine the panel was also glazed on the wet press before the winding up at a pressure of 5.5 kg/sq.cm. 20

Example 3

- 25 The same preparation as in Example 1 was repeated except that no latex was used, and the sheet was glazed at a pressure of 5.5 kg/sq cm, dried and heat-treated at 175°C in the absence of pressure in order to melt at least part of the polyethylene fibrils. 25

Example 4

- 30 An aqueous mixture consisting of 32 kg of high-density polyethylene fibrils similar to those of Example 1, and 14 kg of bleached conifer cellulose was refined at a concentration of 2.5% solids in a conical refiner up to 70° SR. The blend obtained was mixed with 54 kg of silica (Ultrasil VN-2) and then diluted with water to 0.6% solids. 4 kg of Teepol PG were added, the pH was brought up to 5 with aluminium sulphate, and the suspension was used for forming a sheet with a continuous pressure of 2 kg/cm² on a wet press. After drying, the sheet was heated at 175°C in the absense of pressure, in order to melt at least part of the fibrils. 35

Example 5

- 40 An aqueous blend of 27 kg of polyethylene fibrils similar to those of Example 1, and 12 kg of bleached conifer cellulose, was refined in a conical refiner to a 2.5% solids concentration and 70° SR. To this was added 47 kg of silica (Ultrasil VN-2) and, after dilution to 0.6% solids, 28 kg of latex of the acrylic copolymer (DR-1465 Montedison) used in Example 1, and 2 kg of Teepol PG. After acidifying up to pH=4.5 with aluminium sulphate, a sheet was formed by a paper making method, Starting from the dispersion that had been further diluted to 0.2% solids, operating in the continuous wet press, under a pressure of 3 kg/sq.cm. The sheet was dried at about 95°C. 40

Example 6

- 45 There was prepared a mixture of polyethylene fibrils and cellulose fibres as in Example 5, starting from 25 kg of fibrils and 11 kg of cellulose. After refining to 70° SR, the blend was mixed with 9 kg of glass fibres, having a diameter of 10 microns and a length of 6 mm, and then with 41 kg of silica (Ultrasil VN-2). After dilution of the dispersion with water at 0.6%, it was mixed with a further 28 kg of latex of the acrylic polymer (DR-1465 Montedison) used in Example 1, and with 2 kg of Teepol PG. 50 Using aluminium sulphate in a saturated solution, the dispersion was brought to pH=4.5. Then, operating with a final concentration of the dispersion of 0.2% solids, a panel was prepared on the wet press under a pressure of 5.5 kg/sq.cm. The sheet was dried at about 95°C. 50

Example 7

- 55 By means of a conical refiner, an aqueous blend at 2.5% of solids, consisting of 43 kg of polyethylene fibrils as in Example 1, and 19 kg of bleached conifer cellulose, was refined to 67° SR. To the blend thus refined, diluted to a 0.6% solids concentration, there were added 22.5 kg of white talc powder and 31 kg of latex of acrylic copolymer DR-1465 Montedison as used in Example 1. After mixing the dispersion with 2.75 kg of Teepol PG, it was brought to a pH=4.5 with aluminium sulphate 55

in a saturated solution. The preparation of a sheet is carried out on the wet press of the continuous machine operating at a pressure of 1 kg/sq.cm.

Example 8

The preparation of Example 7 was repeated using Ultrasil VN-2 silica instead of talc powder.

5 Example 9

An aqueous mixture of 24.5 kg of polyethylene fibril as in Example 1, but containing incorporated therein 30% of silica, and 10.5 kg of conifer cellulose was brought up to 70° SR. After diluting the fibrous dispersion to 0.6% solids, it was mixed with 17.35 kg of glass fibres of 10 micron diameter and 6 mm length, and then immediately with 32.65 kg of Ultrasil VN-2 silica and 30 kg of latex of the acrylic polymer with 50% solids content used in Example 1. After an addition of 2 kg of Teepol PG, the dispersion was acidified to pH 4.5 with aluminium sulphate solution. After dilution of the dispersion to a 0.2% solids, a sheet was prepared and dried.

Example 10

The preparation of Example 1 was repeated, using however as polymeric latex, 30 kg of polyvinyl chloride latex (Diofan 193d of BASF). The characteristics of the sheet showed only a slight increase in electrical resistance which increased to 1.65 milliohm/sq.dm.

Example 11

Again there was repeated the preparation as in Example 1, except that there were used polypropylene fibrils having a surface area of 2 sq.m/g, a mean fibril length of 3 mm and a mean diameter of 18 microns. The characteristics found were substantially the same as those in Example 1, except the density value which was 0.5 g/cu.cm and the surface area which was 6 sq.m/g.

Example 12

In order to increase the output rate, which is limited by the low ungluing value of the blends or mixes of the preceding Examples, the preparation of a sheet was carried out using a continuous machine with three flat forming tables. The flat tables of the continuous machine were fed with a fibrous dispersion of the same composition as in Example 1. The panel thus produced had the outer layers with a specific weight of 50 g/sq.m. and an inner layer with a specific weight of 60 g/sq.m. The characteristics of the sheet obtained were similar to those of Example 1, except as for the density (increased to 0.540 g/cu.cm) and the porosity in the air (reduced to 28 cu.cm/min). The manufacturing cost was lower by 15% compared with that of a machine with only one single forming plate or table.

Example 13

Using a continuous three-table machine, a panel for separators was prepared, consisting of three layers showing the following composition:

		Outer layer	Inner layer	
35	Polyethylene fibrils as in Example 1	35.5%	15.0%	35
	Bleached cellulose	12.9%	8.5%	
	Glass fibres as in Example 1	8.6%	11.0%	
	Ultrasil VN-2 silica	21.5%	56.0%	40
40	Acrylic copolymer as in Example 1, in the dry state	21.5%	9.5%	

The specific weight of the single layers was about 53.5 g/sq.m. Operating in this way there was achieved a greater retention of filler (silica) in the panel: 93%. The characteristics of the sheet were substantially the same as those of Example 1, except for the electrical resistance which was 1.4 milliohm/dm².

Some of the panels, prepared according to the Examples, were used for producing complete separators, by fitting the panels with spacers by means of direct extrusion. In the cases in which the sheets were subjected to a thermal treatment for the melting of the fibrils, the putting into place of the spacers was carried out by thermowelding the spacers during the heat treatment. The spacers consisted of low-density polyethylene with a heavy charge of talcum powder and a small quantity of carbon black. From the sheets as obtained in Examples 4, 5, 7 and 13, there have also been prepared covers exploiting the thermo-weldability of the materials. The adhesion proved in all instances greater than the tearing resistance of the material.

Properties of Sheets Formed in the Examples

Example No.	1	2	3	4	5	6	7	8	9
Weight (g/sq.m)	160.5	162.3	159.7	171.7	174.3	167	163	154	158.9
Thickness (mm)	0.306	0.277	0.267	0.410	0.390	0.346	0.310	0.330	0.404
Density (g/cu.cm)	0.525	0.586	0.577	0.419	0.447	0.483	0.525	0.468	0.393
Break load (dry) (kg/sq.cm)	84.54	94.11	95.39	—	—	—	—	—	—
Break load (wet) (kg/sq.cm)	23.30	24.08	52.17	—	—	—	—	—	—
Residual Resistance (wet) (%)	27.56	25.59	54.69	—	—	—	—	—	—
Bendsten porosity in air (cc/min)	35	20	35	190	45	50	20	45	260
Max pore dia. (microns)	5.5	4.0	4.9	10	6.2	6.4	5.6	5.4	11.3
Mean pore dia. (microns)	4.1	3.2	3.7	6.7	4.1	4.5	4.0	4.2	8.4
Electrical Res.* (milliohm/dm ²)	1.52	1.55	2.1	1.45	1.3	1.17	2.0	1.05	1.39
Total porosity (%)	68	65	60	65	67	60	65	70	61
Surface area (sq.m/g)	12	—	—	—	—	—	—	—	—
Stiffness (g/cm)	88	80	82	89	—	—	—	—	—

*after 20 minutes immersion in a bath

Claims

1. A process of manufacturing a separator for a lead acid accumulator which comprises making an aqueous dispersion of a blend of cellulosic fibres and olefin polymeric fibrils in a ratio of from 20:80 to 40:60, the blend having a degree of freeness of from 40 to 75° SR, from 20 to 55% of an inorganic powdery material soluble in 30% sulphuric acid at 71°C after 72 hours residence to an extent of less than 5%, and from 0.01 to 0.3% of a wetting agent, and forming a sheet from the dispersion by a paper-making method. 5
2. A process according to claim 1 in which the dispersion contains up to 50% by weight with reference to the blend of glass fibres having a diameter not exceeding 15 microns. 10
3. A process according to claim 2 in which the proportion of glass fibres is from 10 to 20%. 10
4. A process according to any preceding claim in which the sheet is heated under the substantial absence of pressure to a temperature at least equal to the melt temperature of the fibrils.
5. A process according to any of claims 1 to 3 in which the dispersion contains up to 50% of a vinyl or vinylidene polymer, an ethylene, propylene copolymer, or a copolymer of a vinyl or vinylidene monomer with ethylene containing up to 50 mol % copolymerised ethylene. 15
6. A process according to claim 5 in which the proportion of the said polymer or copolymer is from 10 to 20%.
7. A process according to any preceding claim in which the sheet is formed of two layers of different composition.
8. A process of manufacturing a separator for a lead acid accumulator as herein described in any of the Examples. 20
9. A separator manufactured by a process according to any preceding claim.
10. An accumulator containing a separator according to claim 9.